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MEASUREMENT OF CARBON ISOTOPE RATIOS IN VOLATILE HYDROCARBONS DERIVED FROM PLANTS

FINAL REPORT

CRC-APRAC Project No. CAPA-11-71

by

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TABLE OF CONTENTS

		Page
	ABSTRACT	iii
1.0	Introduction	1
2.0	Analytical Procedures	2
3.0	Analytical Results	9
4.0	Comparison of Results With Other	14
5.0	Conclusions	17
6.0	Possible Future Directions	18
	Acknowledgments	19
	References	20

ABSTRACT

Two samples of volatile hydrocarbons from heated (40°C) pine tree needles (Pinus strobus) were collected at dry ice temperature and analyzed to determine their chemical and carbon isotope composition. It was found that the hydrocarbons were mainly α-pinene and β-pinene and the δC^{13} values for the samples were -29.5‰ and -29.8‰, respectively. These isotopic values are in the middle of the range of those from pure terpene compounds derived from commercial sources, namely α-pinene, -22.8‰; β-pinene, -27.4‰; myrcene, -28.7‰; carene Δ 3, -29.3‰; and camphene, -32.6‰. All values for terpene extracts are δC^{13}‰ relative to PDB and were measured at the same time and with reference to the same standards as the hydrocarbons collected from plants.

The observed carbon isotope ratios in volatile hydrocarbons collected from one species of conifer are thus found to be similar to commercial terpene extracts and indicate that significant fractionation probably does not occur during the release of the hydrocarbon from the plant. While the δC^{13} values for effluent hydrocarbons seem to represent the compounds in the plants, the values are within the range of petroleum and petroleum products, so a unique distinction between the two classes of materials cannot be made. Petroleum products have been found to range between -23.0 and -31.8‰, so our original hypothesis that effluent natural hydrocarbons may be identifiable on the basis of distinctive carbon isotope composition does not seem to be substantiated by the two samples measured.

It should be noted that the carbon isotope composition of plants is a result of the biochemical mechanism of photosynthesis. Two distinct groups of plants have been identified. The C_3 plants (Calvin pathway) have δC^{13} values of about -28‰; whereas C_4 plants (Hatch-Slack pathway) have values of about -12‰. Since the pine trees that were the subject of the present study are C_3 plants, the observed δC^{13} values are not surprising. C_4 plants, including some grasses, probably dominated the source of organic material dissolved in surface water in the vicinity of the Texas petrochemical plant, which provided a basis for the hypothesis tested in the present study. The dissolved hydrocarbon δC^{13} values of -15.5 to -24.7‰ were observed to be distinct from petrochemical values and it seemed possible that the distinction would be broadly applicable. It is now apparent that some plants produce hydrocarbons which may be distinguished from petroleum hydrocarbons while others do not. Any future assessment of the origin of airborne hydrocarbons must identify the type of source plants in the area studied if isotopic characterization is to produce meaningful results.

1.0 INTRODUCTION

In Teledyne Isotopes (TI) Proposal No. 25001, submitted to Coordinating Research Council (CRC) in February 1975, we suggested that it may be possible to determine whether airborne hydrocarbons are predominantly natural or man-made by measuring their carbon isotope composition. At a subsequent discussion of the proposal held with the CRC it was decided that the most critical unknown in the problem is whether volatile hydrocarbons from plants have distinctive carbon isotope ratios when compared with petroleum and petrochemical products. Rather than undertake an extensive program for measuring the isotopic composition of airborne hydrocarbons, it was decided to concentrate at this time on the study of hydrocarbon effluent from plants growing under controlled conditions.

In order to obtain samples of effluent hydrocarbons from plants growing under controlled conditions a subcontract was let to Boyce Thompson Institute for Plant Research, Inc. in Yonkers, New York. The facilities at BTI included controlled environment chambers and experience in collecting and analyzing hydrocarbons.

Original plans called for collection of hydrocarbons from a coniferous tree, a deciduous tree, and a grass-soil combination. Difficulties were encountered, however, in finding a collection system that would quantitatively collect hydrocarbons while effectively discriminating against the large volumes of water vapor and carbon dioxide which dominated the effluent stream. The

various unsuccessful approaches to making collections from living plants are described in the following section on Analytical Procedures. The final collection method consisted of warming pine needles to 40°C and passing nitrogen through them in a closed container. Hydrocarbons were collected in a dry ice cooled trap, transported to Teledyne Isotopes, purified, combusted to carbon dioxide and analyzed for carbon isotope composition. The composition of pure terpene extracts was also determined to provide a basis for interpreting the data from the effluent volatiles.

2.0 ANALYTICAL PROCEDURES

The analytical procedures consisted of two parts, sample collection and chromatographic analysis carried out at BII and carbon isotope analysis carried out at TI.

2.1 Sample Collection

The objectives of this project were to collect and partially characterize the total volatiles emanating from living plants. Pine trees were chosen for the initial studies, since these were expected to produce the largest quantities of volatiles.

The potted pine trees were placed in a chamber, 31 x 24 x 23 in., of 1/4 inch methacrylate. This chamber was kept within a controlled environment chamber which provided constant light and temperature conditions along with charcoal-filtered air. An additional charcoal filter was fitted to the inner chamber, and the incoming air was passed over the plants to an exit port where the collection devices were attached. A flow rate of approximately 1.8 ℓ /min was obtained using the house vacuum line.

Porapak collection

Glass columns, 1/2 in. diameter and 10 in. long were manufactured with ground glass ends to facilitate transfer of collected material without the use of plastic tubing. The columns were filled with Porapak Q and attached to the exit port of the chamber. Air was drawn through the chamber and the Porapak column for different time periods, and the volatiles were eluted from the Porapak by nitrogen at a temperature of 140°. The columns were connected to transfer tubes and cold traps by means of ground glass joints. The eluted material was collected in traps cooled with liquid nitrogen and monitored by gas chromatography using a 15% FFAP column at 60° and 120°. Breakthrough times were measured in the laboratory using methanol and α-pinene as test compounds. These experiments showed that methanol had a breakthrough time of less than 1 hour and α-pinene about 8 hours at a flow rate of 100 ml/min of nitrogen. Analysis of the volatiles eluted from Porapak revealed the presence of many artifacts. Most of the collected material appeared to be from the Porapak itself. Extensive conditioning of the Porapak at elevated temperatures did not appear to help. Solvent washing of the Porapak removed large quantities of volatiles, but difficulty was encountered in removing all the solvent. Heating after solvent washing again introduced extraneous volatiles. We concluded that Porapak Q is not sufficiently stable for this kind of study where the introduction of volatiles from non-plant sources must be avoided.

Tenax collection

Tenax is a porous polymer which is reported to be highly stable at elevated temperatures. Washing with solvents showed that no UV-absorbing materials were eluted and no volatiles were detected by gas chromatography. However, columns packed with Tenax gave very short breakthrough times. Also the breakthrough times were greatly reduced in the presence of water. When a column was attached to the chamber, α-pinene broke through in less than 1 hr. The capacity of Tenax appears to be limited, and the large quantities of water released during transpiration by the plants present a major problem in this approach.

Charcoal collection

Attempts were made to determine whether the plant volatiles could be collected on activated charcoal and recovered by heat desorption. However, only partial recovery of the collected material was obtained.

Cold trap collection

A system of traps was set up using both dry ice and liquid nitrogen as coolants. The experiments showed that dry ice traps are not sufficient to remove all the volatiles, and the use of liquid nitrogen is complicated by the collection of carbon dioxide.

Conclusions

Our attempts to collect volatiles from plants in sufficient quantities for carbon isotope ratio measurements in a way that avoids the introduction of volatiles from any other source have served to demonstrate many of the problems involved in meeting these goals. Many techniques are available,

but most of these are selective for a particular group of the volatiles. One of the most formidable problems is the removal of the large quantities of water and carbon dioxide released by plants along with minute quantities of organic volatiles. A new system for removal of water has been introduced by Perma Pure Products, Inc. These Perma Pure dryers are capable of removing water from most gas streams, but also remove polar organic compounds. If the studies on plant volatiles could be confined to hydrocarbons, then this system might be considered.

Probably the best approach to this problem would be to use a combination of cold traps and Tenax columns, with frequent recycling. The air entering the plant chamber should be brought from a separate area which has a normal carbon dioxide level. Much of the water might be removed by a cold water condenser before leaving the chamber. Dry ice traps might then be backed up by Tenax columns which could be changed frequently. The collected material could then be recycled through Tenax until enough water has been removed. This operation would require a considerable investment in time and materials.

Compromise plan

At a meeting of the CRC-APRAC Project Group CAPA - 11/15 in Detroit on October 6, 1976, these results were presented, and a final course of action was considered. A proposal to collect the volatiles from pine needles in the laboratory was accepted as a last effort.

Headspace samples from pine needles and from a plastic bag covering the foliage of a live pine tree were compared by gas chromatography to determine the validity of this approach. The same major volatile components were detected in both samples: i.e.; α-pinene and β-pinene from Pinus strobus.

Needle samples from white pine trees growing in North Yonkers were taken during early November 1976, cut into short lengths and weighed. Samples of 25-50g were processed for each collection of the volatiles. The needles were maintained at 40°C in a flask by means of refluxing methylene chloride. Nitrogen gas was passed through the bed of needles at a rate of 100ml/min, and the vapors in the nitrogen stream were collected in a trap cooled in dry ice for a total period of 5 hours. The contents of one trap were washed out with ethyl ether for gas chromatographic analysis. The quantity of terpenes present was estimated to be greater than 10mg, based on comparison with a standard solution of α-pinene. These samples were, therefore, considered to be adequate for carbon isotope analysis, provided that the water present would not present a problem.

2.2 Carbon Isotope Analysis

The samples of effluent hydrocarbons described in Section 2.1 above were delivered to TI on December 2, 1976. The samples were delivered packed in dry ice after having been stored in a freezer subsequent to collection. The samples were introduced into a combustion system consisting of a dry ice trap, a plain glass LN_2 trap, and a combustion furnace which utilizes CuO at 700°C to catalyse the combustion of hydrocarbons to CO_2 in an O_2 atmosphere.

The sample, presumed to be free of CO_2 which had been eliminated in the collection process, was contaminated only with water which did not interfere with the carbon analysis. The condensible part of the sample was frozen out in the dry ice trap. All air was then pumped away and 0.5 atmospheres of O_2 was introduced into the combustion system. The sample was warmed and circulated through the combustion furnace where the hydrocarbons were converted to CO_2. Water present in the sample and produced by the combustion was removed on the dry ice trap and the CO_2 was collected in the LN_2 cooled trap. The CO_2 was then transferred to a collection vial and taken to the mass spectrometry laboratory for analysis.

The CO_2 sample was analysed mass spectrometrically using CO_2 generated from the NBS-20 standard as a reference gas. The two samples supplied were analysed in the same way.

In addition to the two samples of collected effluent hydrocarbons five pure terpene extracts were analysed in duplicate along with two NBS standards, also analyzed in duplicate.

The mass spectrometric analyses were carried out on a Nuclide Corp. RMS-60 ratio mass spectrometer using techniques similar to those described by Craig [4]. During the course of the measurements we measured the standard reference material NBS-21 (graphite) and NBS-22 (oil) and found a positive δC^{13} bias of about $0.6^{0}/_{00}$ in our measurements. To make our reported values agree better with other published values, all our measurements have been corrected by subtracting $0.6^{0}/_{00}$ even though this bias is close to our stated analytical precision of $\pm 0.5^{0}/_{00}$.

In order to verify that the samples were not contaminated by CO_2 from the dry ice in which the samples were packed, the CO_2 from the dry ice was analyzed. Since a value of $\delta C^{13} = -51.9$ was obtained which is quite distinct from all other values measured, it is concluded that the samples were free from contamination from that source.

5.0 ANALYTICAL RESULTS

The analytical results from the study of the carbon isotope composition of plant-derived hydrocarbons are presented in Table I along with appropriate Standard Reference Material analyses.

The commercial terpene extracts are limited in their applicability to the study because the details of processes employed in their production are not known. The fact that the two hydrocarbon effluent samples fall in the middle of the range for the hydrocarbon extracts and, in fact, are almost indistinguishable from three of the five extracts studied, however, strongly suggests a correspondence between the two materials. The interpretation of these data in relation to the data of other studies is discussed in the following section.

TABLE I

	Measured Values δC^{13} (‰) PDB	Corrected Value (Measured minus 0.6‰)
Commercial Terpene Extracts		
α-Pinene	-28.1, -27.5	-28.4
β-Pinene (undistilled)	-22.5, -22.1	-22.8
Myrcene	-28.1, -28.0	-28.7
Carene A-3	-28.6, -28.7	-29.3
Camphene	-32.3, -30.6	-32.6
Volatile Hydrocarbons Collected from Pine Needles		
Sample Collected 11/5/76	-29.2	-29.8
Sample Collected 11/7/76	-28.7	-29.3
Standard Reference Materials	This Study δC^{13} (‰)	Accepted Value
NBS-21 (Graphite)	-27.5, -27.1	-27.79
NBS-22 (Crude Oil)	-28.9, -28.8	-29.4
Special Test Sample		
CO_2 from Dry Ice	-51.9	

4.0 COMPARISON OF RESULTS WITH OTHER STUDIES

The present study was undertaken to determine whether volatile terpene hydrocarbons derived from plants would have a distinctive carbon-isotope composition with respect to petroleum and petrochemical products. The data from two samples suggests that the carbon isotope composition of effluent hydrocarbons is not significantly different from that of extracts of pure compounds derived from similar plants. In order to place these results in perspective and assess whether they can be used to identify the source of airborne hydrocarbons we must examine the published carbon isotope values for plants and for petroleum products.

The typical ranges of carbon isotope values are shown in Figure 1, along with the results of the present study. Calder and Parker[2] found that it was possible to distinguish between natural hydrocarbons and materials from a petrochemical plant on the basis of carbon isotopic composition. The range of δC^{13} values found in an unpolluted natural system was -15.5 to -24.7‰ with a one year average range of -17 to -22‰. They found that the least negative value for petrochemicals was -25.9. Thus there was minimal overlap of the two classes of materials and carbon isotope ratios were useful in assessing the degree of pollution from artificial sources. The pertinent data from this study are included in Tables II and III.

On the basis of these observations it was hypothesized that δC^{13} values less negative than about -22‰ might be generally characteristic of volatile hydrocarbons derived from plants even though it was recognized that values in the range of -24 to -30‰ were typical of land plant material as a whole.

δC^{13} VALUES FOR COMMERCIAL TERPENE EXTRACTS & EFFLUENT VOLATILES FROM PINUS STROBUS

PUBLISHED δC^{13} VALUES FOR VARIOUS CARBON RESERVOIRS

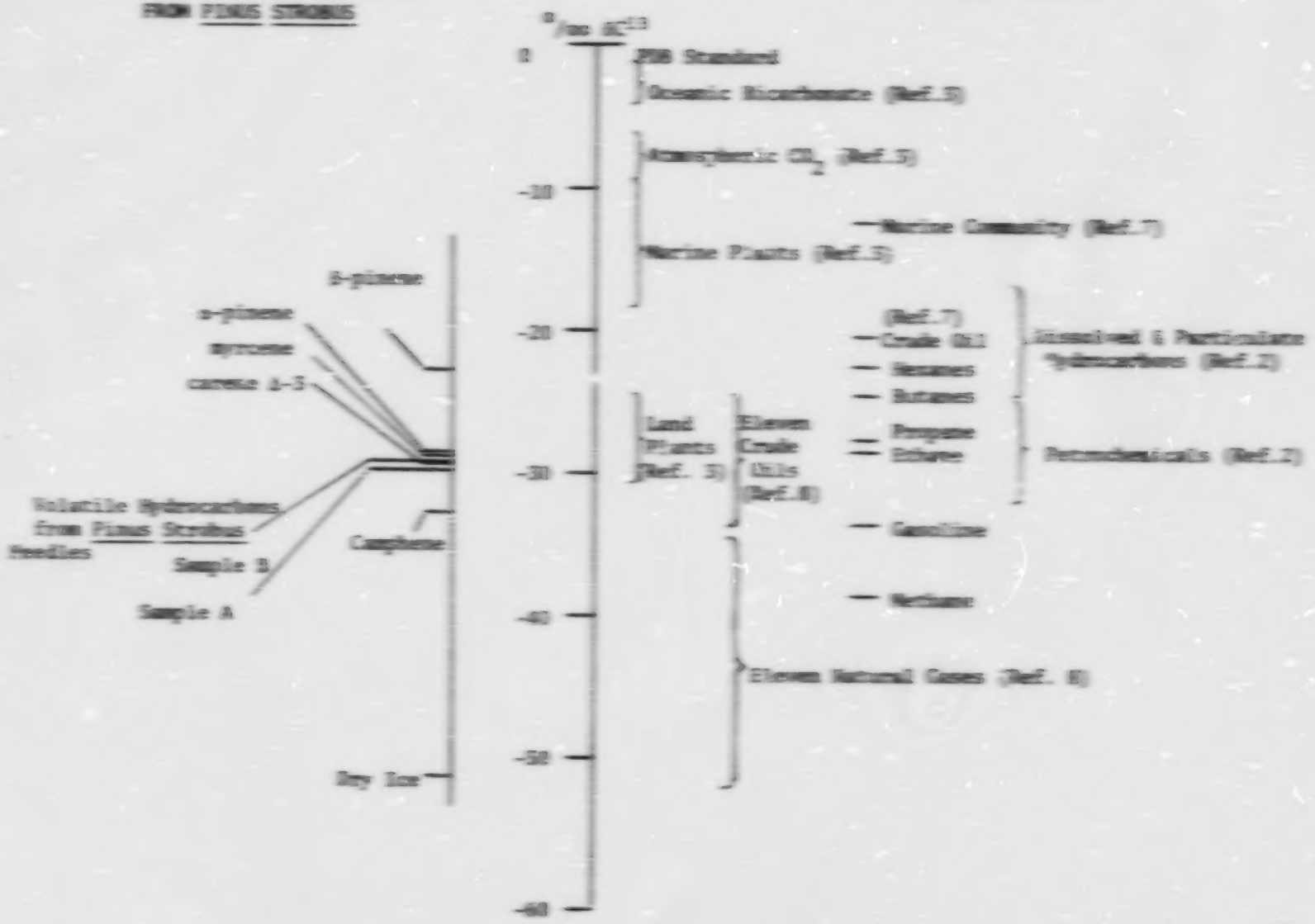

FIGURE 1

TABLE II

ΔC^{13} of Materials from a Texas Petrochemical Plant[1]

Sample	ΔC^{13}
Natural Gas Master Inlet	-31.6
Ethylene	-27.8
Propylene	-29.3
Acetylene	-26.0
High-density Polyethylene I	-28.4
High-density Polyethylene II	-30.1
Low-density Polyethylene	-29.2
Styrene	-28.0
Cellosolve	-29.3
Ucon Oil	-23.0
Monoethylene Glycol	-30.4
2-Ethylhexanol	-31.6
Isobutyl Alcohol	-26.0
Aromatic Mixture	-31.6

ΔC^{13} is in units of $^0/_{00}$

TABLE III

δC^{13} of Dissolved Organic Matter

in the Vicinity of a Texas Petrochemical Plant (2)

Sample	δC^{13}
River Water Intake	-19.6
River Water Intake	-20.1
River Water Intake	-17.7
Barge Canal	-15.5
Adjacent Bay	-15.6
Adjacent Bay	-24.7
Adjacent Bay	-19.9
Gulf of Mexico	-21.7

The δC^{13} values for two samples of volatile hydrocarbon collected from Pinus strobus needles and the correlative data from terpene extracts shows that they are distinct from the -17 to -22°/oo range found by Calder and Parker[7] for dissolved hydrocarbons. The question thus arises as to why the hydrocarbons we studied are different from those studied by Calder and Parker.

An increasing amount of work has been done in recent years on tracing the pathways of biosynthesis using carbon isotopes and the distinction between the measurements of the present study and the data of Calder and Parker seem to be understandable in terms of the different plants studied.

Lerman and Queiros[6] have provided the following explanation:

> "In particular, isotope analyses have proved convenient for differentiating plants(9,10) which photosynthesize via the enzyme ribulose-1,5-diphosphate carboxylase (RuDPC) (the Calvin, or C_3, pathway) from plants which photosynthesize via the enzyme phosphoenolpyruvate carboxylase (PEPC) (the Hatch-Slack, or C_4, pathway(11))."
>
> " The carbon fixed by a terrestrial plant has lower ^{13}C and ^{14}C concentrations than the atmospheric CO_2. This depletion is due to isotope discrimination or fractionation."
>
> "Two distinct groups can be observed with modes at about -12 per mil, on the δC^{13} scale(13),for the C_4 plants and -28 per mil for the C_3 plants. The composition of the free atmosphere on the same scale is about -6.7 per mil(12)."

Since Pinus strobus is a C_3 type plant, the hydrocarbon compounds have the characteristic -28°/oo δC^{13} values which are also exhibited by the terpene compounds produced by similar plants. Since the terpenes are rather heavy ($C_{10}H_{16}$) and have very small range of boiling points (154° - 167°C, α-pinene to myrcene) it is unlikely that isotopic fractionation occurs as a physical process during the evolution

of volatile effluents. It is more likely that the isotopic characteristics are set by the biosynthetic mechanism which produces the compound.

Because of the small quantity of effluent available for collection, we were, unfortunately, unable to extend the study to include deciduous trees and grasses as was originally planned. Had some C_4 type plants been successfully sampled, our results might have shown a quite different range of δC^{13} values similar to those found in natural systems by Calder and Parker[2].

We must now say that hydrocarbons produced by C_3 type plants probably will not be distinguishable from petrochemical products but the possibility remains that hydrocarbons from C_4 type plants probably would be distinguishable. The question must be addressed by other studies being carried out by the CRC as to what is the relative quantitative importance of hydrocarbon effluents from C_3 and C_4 type plants. If C_3 type plants are the dormant source of airborne hydrocarbons, then the attempt to distinguish them from petroleum derivatives should be abandoned. If C_4 type plants are the dominant source, then isotopic characterization may yet prove to be a fruitful approach to quantifying the relative importance of natural hydrocarbons to the overall atmospheric burden. Since there may be regional variations in the relative abundance of the two types of plants, some areas may be more appropriate for study than others.

5.0 CONCLUSIONS

The conclusions from the study of the carbon isotope composition of volatile hydrocarbon effluents from Pinus strobus and of terpene extracts are summarised as follows:

1) δC^{13} values for volatile hydrocarbons evolved from needles of Pinus strobus at a temperature of 40°C are about -29.5 and fall within the range of terpene extracts which is -22.8 for β-pinene (undistilled) to -32.6 for camphene.

2) The observed δC^{13} values for terpene extracts and volatile hydrocarbons fall in the same range as a variety of petrochemical products and are, therefore, from an isotopic standpoint, indistinguishable from them.

3) The observed isotopic ratios are characteristic of C_3 type plants and different results would probably be obtained if the study were extended to C_4 type plants.

4) Observations of hydrocarbons in natural systems in the range of δC^{13} -17 to -22‰ which probably suggested the present study probably arose from the presence of C_4 type plants in the environment.

6.0 POSSIBLE FUTURE DIRECTIONS

1) Further study of the applicability of carbon isotope ratio measurements to assessing the relative quantitative presence of natural airborne hydrocarbons is possible but should be preceded by study of the relative importance of C_3 type vs. C_4 type plants in the area to be studied.

2) The problems of dealing with the collection of small amounts of hydrocarbons in the presence of large amounts of water and carbon dioxide may be solved by design of systems to sample specific compounds rather than attempting a total composite sample as was done in the present study. A system would have to be designed for working directly with the output of chromatographs which would allow specific identification of the compounds to be measured, coupled with miniaturization of the combustion and mass spectrometer inlet system to permit handling 0.1 cm^3 or smaller samples.

3) One of the main problems with the collection system tried in the present study was the attempt to quantitatively trap hydrocarbons on columns of limited capacity. It may be possible to design a flow-through system which quantitatively traps CO_2 and water vapor and allows the hydrocarbons to enter a combustion chamber where they are converted to CO_2 and then trapped. Since specific chemical reactions for H_2O and CO_2 are possible, high retention capacity may be achievable without significant loss of the hydrocarbons of interest.

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The design, construction and operation of the sample purification and combustion system by Mr. Davis Rieman was also a major contribution to the project.

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